PROPERTIES AND APPLICATIONS OF Cu-BASED SILVER FREE BRAZING FILLER METALS MADE BY RAPID SOLIDIFICATION TECHNIQUE

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ABSTRACT

Technical and commercial interest in silver-free brazing filler metals (SFBM) is directly related to the fact that they are at least twice cheaper than silver filler metals. A Rapid Solidification method was developed to manufacture cost-effective SFBM in the form of rods, wires, and strips. Principles of this method are presented in the paper, and the properties of the brazing filler metals are discussed.

Some of these SFBM such as P81 and P14 of the Cu-Zn-P-Ni and Cu-P-Sn systems and P21 of the Cu-Zn-Sn system are qualified as the full value substitutes of silver alloys in the manufacture of both copper and steel brazed structures. Another one filler metal P47 belonging to the Cu-Zn-Mn system was also successfully used for brazing cemented carbide tools.

The P81 and P14 filler metals have the same brazing temperature range as 40-50% silver alloys and provide sufficient shear strength of 19-21 ksi (132-148 MPa) for copper brazed joints, 16-20.6 ksi (110-142 MPa) for brass joints, and about 18 ksi (125 MPa) for steel-to-steel joints (P81 only). The tensile strengths of these brazed joints are significantly higher. However, the brittle iron-phosphides affect impact strength of the steel joints.

In order to avoid this negative effect and eliminate phosphorus from the alloy compositions, the P21 and P47 were redesigned and are being used for making steel joints and carbide tools by induction and torch brazing. Stainless steel joints brazed with the P21 filler metal have a shear strength of 21 ksi (147 MPa), while steel joints brazed with the P47 filler metal exhibit higher shear strength of 23 ksi (157 MPa). The tensile strength of low-carbon and stainless steels made by the filler metal P47 is extremely high – in the range of 42-45 ksi (292-312 MPa).

The primary target of rapid-solidified silver-free brazing filler metals is the manufacture of cutting and mining tools, stator windings of electric engines, copper tie of transformers, cars, refrigerators, air conditioners, gas heaters, welding torches, thermal sensors, and others.

1. Identification and Significance of the Problem

Technical and commercial interest in silver-free brazing filler metals (SFBM) relates directly to their low cost. The cost of silver-free alloys is about half of that of alloys with 15 wt.% of silver, and 3-5 times cheaper than alloys containing 40-50 wt.% of silver. Many attempts have been made in the last 40 years to substitute silver to cut expenses in brazing production. All of these substitutes were developed and produced using a classic technology: casting ingot and hot extrusion of rods, wires, or strips. Recently, ALARM CORP. (Russia) and METGLAS, Inc. (USA) proposed technologies to produce rods, wires, and thin foils by rapid solidification or melt spinning directly from the melt in order to avoid the expensive hot extrusion process.

Most of the conventional silver-free alloys that could provide a comparable strengths have brazing temperature ranges significantly higher than silver alloys. Only phosphorus-containing SFBM have the brazing temperature in the range of 600-750°C (1110-1380°F) comparable with silver alloys, but these phosphorus alloys produce lower strength of brazed joints, especially in steel joints. Cadmium is still used to depress the brazing temperature of some standard silver alloys, but nowadays, this cancer suspected element is not permitted in new developments.

Another important property of silver alloys is their plasticity in wire and strip forms: this plasticity also allows the fabrication of different preforms (rings, shims, tablets, etc.) from silver brazing alloys. Most customers use silver alloys only as preforms to increase productivity during assembling and brazing. Existing silver-free alloys do not possess sufficient plasticity at room temperature and require hot deformation to produce preform shapes. Hot deformation makes the manufacture of silver-free performs so expensive that they loose a significant part of their cost effectiveness.

Metglas® or melt spinning technology resolved this problem only partially. Preforms can be produced from amorphous foil for limited applications, because the thickness of the foil is 0.002-0.004" (0.05-0.1 mm). Often, such preforms do not have enough metal to fill standard brazing gaps. They can be used only for furnace brazing as filler elements placed between brazed parts.

The brazing filler metals represented in this paper can be considered as a new class of silver-free alloys suitable for brazing not only copper and brass but also for brazing steels and cemented carbides in a wide range of processing temperatures from 650°C (1200°F) to 900°C (1650°F).

2. Method of rapid solidification by extraction from the melt

Copper-based brazing filler metals that cannot be produced by traditional “casting + cold rolling” technologies were manufactured by high speed extraction from the melt using the method developed by Alarm Corp. [1, 2]. This method includes a continuous extraction of the rod (wire) or strip from the bath of molten alloy by a speedy-rotated copper disk - crystallizer. The extracted alloy is immediately solidified on the surface of the cold crystallizer, separated from the crystallizer, and finally wound in the bundle.

The rapid-crystallized wire or rods have asymmetric, not round cross-section due to different conditions of cooling across the disk surface. The non-traditional shape of the wire and rods does not cause any changes in manual operations during brazing. Moreover, the groove along the rods is suitable for making flux-cored brazing filler metals which are already popular in the industry.

The high rate of solidification (10^4-10^5 K/s) results in chemical and microstructure uniformity of the solid product. Brittle phases (phosphides and other intermetallics) are presented as very fine crystals dispersed in solid solutions. This type of microstructure facilitates further processing of the filler metals by plastic deformation to manufacture round rods, wire, or flat strip.

The most important outcome is that the microstructure of the joints brazed by rapid-solidified filler metals is also uniform, without pores or cavities. Such microstructure improves the quality and strength of brazed joints as we will show below. A number of brazing filler metals in the form of wire or strip of the Cu-P-Sn, Cu-Zn-P-Ni,, Cu-Zn-Sn, and Cu-Zn-Mn systems are manufactured today in industrial scale using the established technology of rapid solidification.

A specific meta-stable micro-structure of rapid-solidified products with the grain size <10 μm is formed due to high rate of cooling. For instance, a comparison of cast and rapid-solidified filler metals P14 (Cu-P-Sn) clearly shows the advantage of the melt-quenched quasi-eutectic structure which consists of the saturated solid solution with uniformly distributed copper phosphide phases (Fig.1).

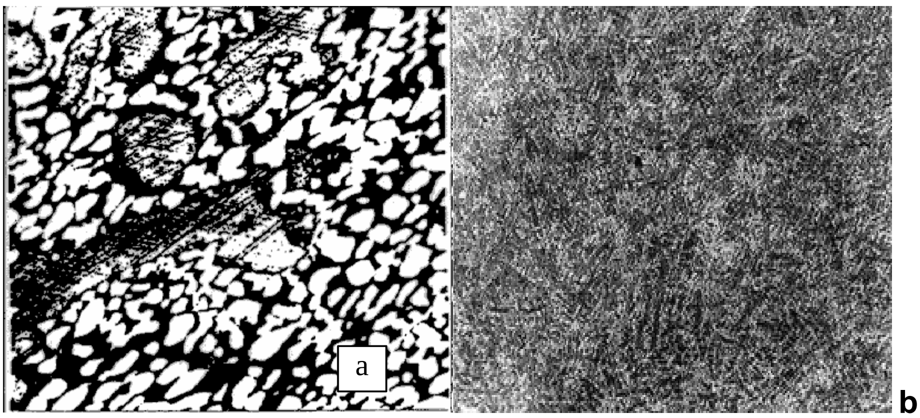

Fig. 1 Microstructure of the brazing filler metal P14 (Cu-P-Sn):
a – cast, x200, and b – rapid-solidified on copper disk, x400

The wires and strips of the rapid-solidified filler metals exhibit much better plasticity than that as-cast products due to smaller phosphides which are uniformly dispersed in the alloy microstructure. The same effect takes place in all other rapid-solidified Cu-based brazing filler metals. Brazing filler metals manufactured today by the above described technology are presented in Table 1.

Table 1

Melting and brazing temperatures of rapidly solidified filler metals

Brazing filler metal	Alloy system	Base metals to be brazed	Melting temperature range	Brazing temperature range
			°C (°F)	°C (°F)
P14	Cu-P-Sn	Copper, Brass	640-680 (1184-1256)	720-800 (1328-1470)
P81	Cu-Zn-P-Ni	Copper, Brass, Steel	630-660 (1166-1220)	680-800 (1256-1470)
P21	Cu-Zn-Sn-Ni		780-830 (1436-1526)	850-900 (1562-1652)
P47	Cu-Zn-Mn-Ni	Copper, Brass, Steel, Cemented carbides	765-815 (1410-1500)	830-900 (1526-1652)

3. Silver-free brazing alloys of the Cu-Zn-P-Ni and Cu-P-Sn systems

Near-eutectic, low-melting brazing filler metals are represented by two alloys: P14 of the Cu-P-Sn system doped with zirconium, and P81 of the Cu-Zn-P-Ni system. These filler metals are especially attractive due to their low melting points (Table 1) and brazing temperatures below 700°C (1290°F).

The brazing filler metal P14 is pretty plastic as manufactured, directly after rapid solidification in the form of 2-4 mm (0.08-0.16 in.) wire. It can be used both as rods and coiled preforms for torch and furnace brazing. The microstructure of brazed joints made with this filler metal is shown in Fig. 2.

The brazing filler metal P81 is brittle as manufactured directly after rapid solidification in the form of 3-5 mm (0.12-0.20 in.) rods. The brittleness in the rapid-solidified state resulted from complex phosphide phases of such alloy components as copper, nickel, and zinc. One of these phosphide phases has a lamellae morphology and affects adversely the bend loading resistance.

The filler metal P81 can be used as manufactured in the form of rods or wires for torch and induction brazing. However, a short annealing for 10-15 min at ~600°C (1110°F) significantly improves the plasticity of the rapid-solidified alloy due to coagulation of above-mentioned lamellar phosphides and destruction of dendrites. Coiled wire preforms can be made from annealed filler metal P81 to be used for induction or furnace brazing as well as for automatic torch brazing.

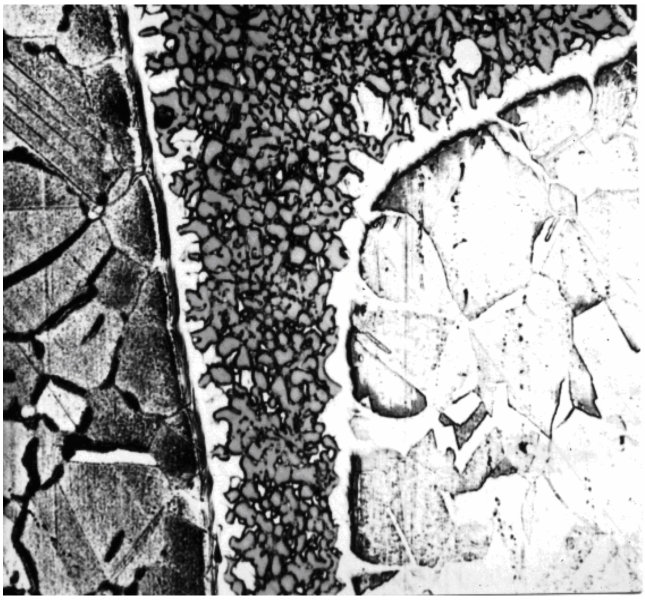

Fig.2 Microstructure of a copper-to-brass joint brazed by the filler metal P14. x50

The microstructure of brazed steel joints made with this filler metal is shown in Fig. 3.

Strengths of copper brazed joints made with the low-melting brazing filler metals P14 and P81 is the same as that of joints made with silver alloys (Fig. 4). Moreover, the tensile strength of brass joints made with P14 is higher by 40% than that of joints brazed with PSr-40 (Cu-40Ag-17Zn-27Cd), while the shear strength of both filler metals is almost the same.

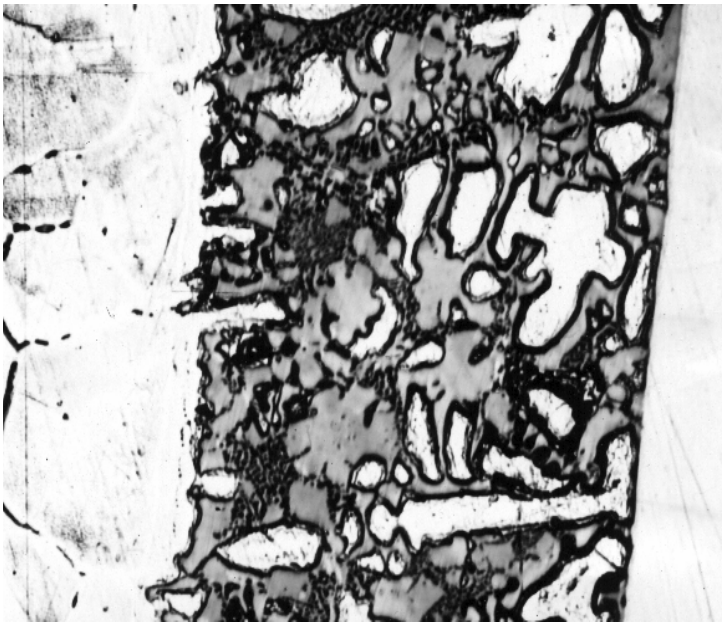

Fig. 3 Microstructure of a brass-to-steel joint brazed by the filler metal P81. x120

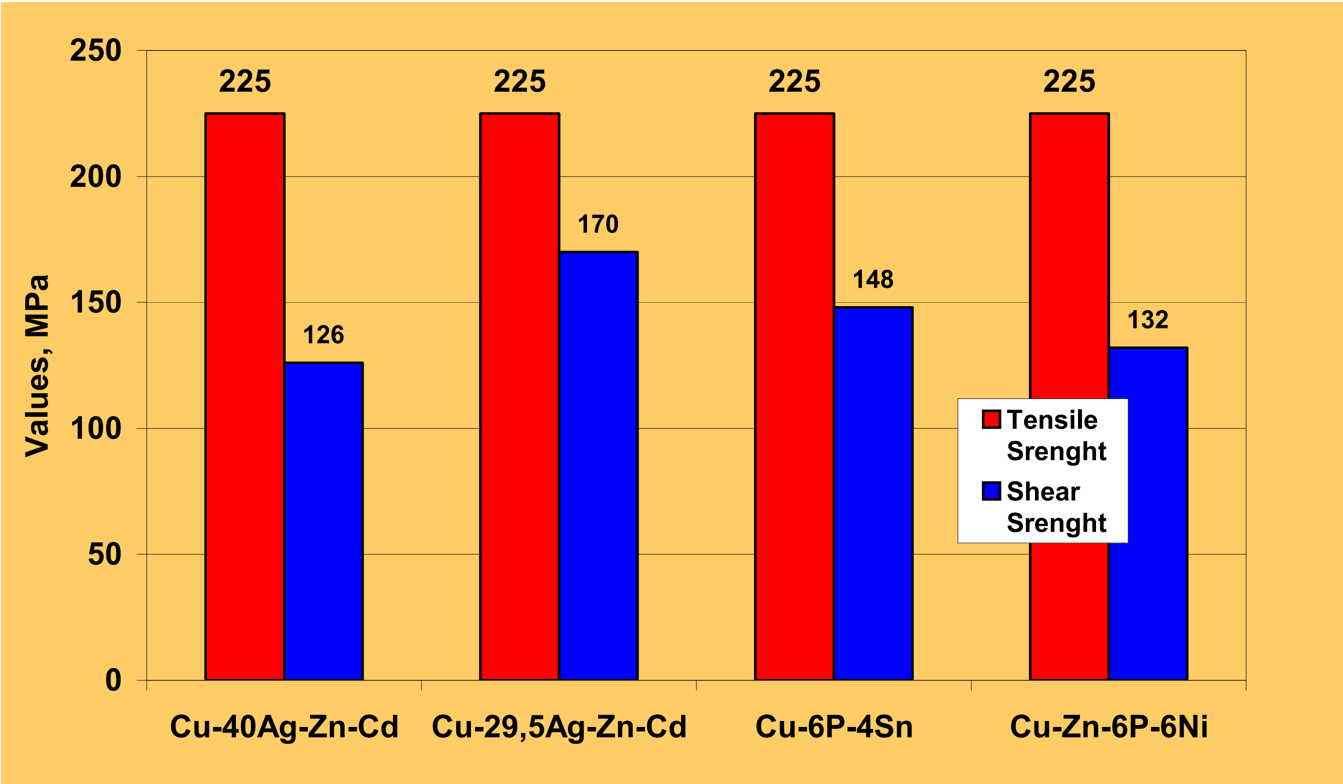

Fig. 4 Comparative strength of copper-to-copper joints brazed by silver-free filler metals P14 (Cu-6P-4Sn) and P81 (Cu-Zn-6P-6Ni) and silver filler metals

4. Silver-free brazing alloys of the Cu-Zn-Sn-Ni and Cu-Zn-Mn-Ni systems

Brazing filler metals P21 and P47 of the Cu-Zn-Sn and Cu-Zn-Mn systems were developed for joining carbon steels, stainless steels, and cutting tools with cemented carbides [2]. Both these compositions relate to multi-phase brass alloys, which are characterized by low plasticity in the cast state. The brazing temperature of these alloys is higher than that of standard silver filler metals, but it is lower than typical brass-based filler metals. This is especially important in brazing copper to steel or steel to cemented carbides in order to avoid overheating above 900°C (1650°F) that is critical for many steel structures.

Practically, only our rapid solidification technology enables to manufacture such filler metals by an economically effective way because of their low “as cast” deformability. Moreover, melt quenching of the P21 composition resulted in a single-phase microstructure of β–brass, while its cast structure comprises three phases α–, β-, and γ-brass (Fig. 5). The single β–brass structure has essentially better plasticity than that of the cast or hot pressed products and allows to adjust the wire diameter by homogenization and extrusion.

Besides, a homogenizing annealing occurs without the grain growth.

a b

Fig. 5 Microstructure of the filler metal P21:
a – multi-phase “as cast” structure, x200;
b – single-phase rapid solidification structure, x800.

The brazing filler metals P21 and P47 exhibit the best strength when brazing carbon or stainless steel (Fig. 6). A special feature of the brazing filler metal P47 is that this copper-zinc-manganese alloy holds an intermediate position between Cu-Zn and Cu-Mn alloys. This alloy has the lowest melting point among all known silver-free and phosphorus-free filler metals due to high content of manganese. It is manufactured and can be applied in the form of strip, wire, or brazing paste.

The P47 is effective in brazing cemented carbide inserts to wood cutting saws, diamond bits in the copper-nickel binder, various cutting tools for machining, and some types of mining drill bits. The shear strength of brazed joints of the low-alloy steel 35KhGSA is in the range of 200-230 MPa (29-33 ksi). The filler metal is strong and rigid; therefore, a special attention should be paid to the width of brazing clearances.

The filler metal P47 was recommended for brazing cemented carbides and cermets containing titanium carbides and tantalum carbides. Relatively low melting point makes it possible to braze such materials at lower brazing temperature and avoid cracking of carbide inserts susceptible to thermal stresses.

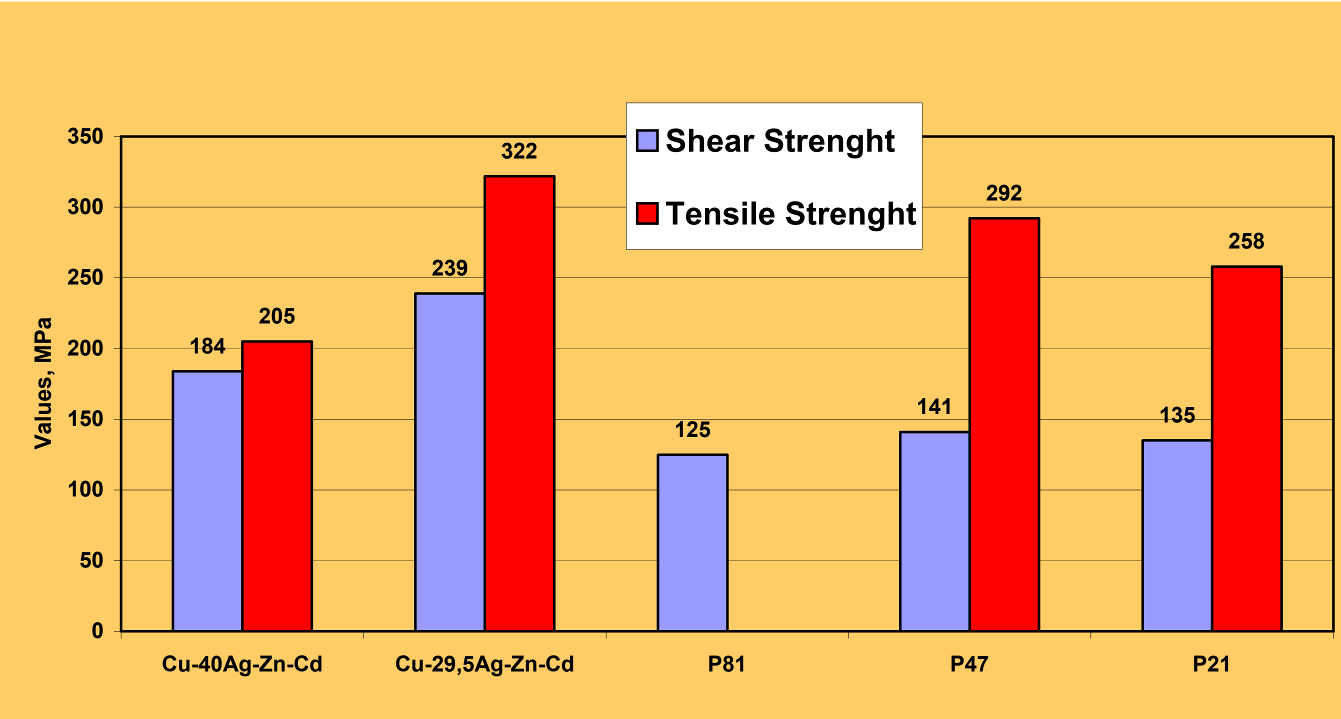

Fig. 6 Comparative strengths of carbon steel joints made by silver-free brazing filler metals P21 and P47 and silver filler metals

5. Applications of rapid-solidified brazing filler metals

The rapid-solidified silver-free brazing filler metals exhibit quite high level of technological, mechanical, and service properties. Therefore, they are successfully used in many applications such as brazing parts of refrigerators, heat exchangers, manometers, electric devices and power supply equipment, welding torches, cryogenic evaporators, cutting tools, and others.

For example, the corrosion resistance of copper tubing joints brazed with the P14 filler metal in the manufacturing refrigerators is the same as that of the Ag-Cu-Zn-Cd filler metals, and besides, the fatigue strength of brazed joints is better than the strength of copper tubes. Also, the filler metal P14 possess the specific electric resistance (0.34×10^{-6} Ω·m) close to that of standard silver filler metals BAg-5 or BCuP-5, and it is successfully used for brazing electric copper cables and high current density buses.

The filler metal P81 is very successful for brazing brass to steel, the P21 – for brazing stainless steel parts, and the P47 – for brazing heavy-loaded cutting tools such as stamping punches or mining drill bits of cemented carbides. Some examples of brazed parts are shown in Figs. 7 and 8.

Fig. 7 Parts of manometers brazed with P81 and P14 alloys (brass-to-steel and copper-to-brass joints)

Fig.8. Parts of torches brazed with the filler metal P14

6. Conclusions

1. Rapid solidification by extraction from the melt is an efficient and economical method to manufacture wire, rods, and strips of the Cu-based silver-free brazing filler metals. These products are successfully used in many industrial applications.
2. The unique microstructure of rapid-solidified brazing filler metals of the Cu-P-Sn, Cu-Zn-P-Ni, Cu-Zn-Sn, and Cu-Zn-Mn systems results in perfect formation of dense, fine-grained structure of brazed joints.
3. Wire and rods of these rapid-solidified brazing filler metals are suitable for further processing by thermal short-cycle homogenization, drawing, extrusion, making flux-cored rods, and so forth.
4. Mechanical and service properties of brazed joints made with the rapid-solidified filler metals response to different application requirements. The brazing filler metal P14 is recommended for joining copper and brass, the P81, P21, and P47 – for joining both copper alloys and steels. The brazing filler metal P21 is especially recommended for joining stainless steel parts, and the P47 – for making carbide cutting tools.

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